

U.S.S.N. 04/689,632
Group Art Unit 1772



Eur päisches
Patentamt

European
Patent Office

Office eur péen
des brevets



Bescheinigung

Certificate

Attestation

RECEIVED

NOV 05 2002

TC 1700

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

99203378.7

Der Präsident des Europäischen Patentamts;
Im Auftrag

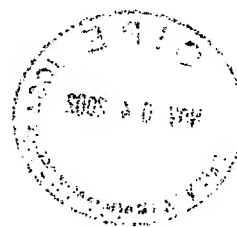
For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

DEN HAAG, DEN
THE HAGUE, 16/06/00
LA HAYE, LE

2000 1 1



THIS PAGE BLANK (USPTO)



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

**Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation**

Anmeldung Nr.:
Application no.: 99203378.7
Demande n°:

Anmeldetag:
Date of filing: 15/10/99
Date de dépôt:

Anmelder:
Applicant(s):
Demandeur(s):
AGFA-GEVAERT N.V.
2640 Mortsel
BELGIUM

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:
Liquid crystal alignment layer

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat:
State:
Pays:

Tag:
Date:
Date:

Aktenzeichen:
File no.
Numéro de dépôt:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:
G02F1/1337

Am Anmeldetag benannte Vertragsstaaten:
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE
Etats contractants désignés lors du dépôt:

Bemerkungen:
Remarks:
Remarques:

THIS PAGE BLANK (USPTO)

15. 10. 1999

- 2 -

[DESCRIPTION]

(54)

FIELD OF THE INVENTION

The present invention relates to a liquid crystal alignment layer. More specifically the invention is related to an oriented polythiophene layer which may be used as a liquid crystal alignment layer and, optionally, also as an electroconductive layer in liquid crystal displays.

BACKGROUND OF THE INVENTION

Liquid crystal displays (LCDs) typically contain a display cell consisting of two sandwiched substrates which each carry at their inner surface a patterned electroconductive layer and a liquid crystal alignment layer. These substrates are kept apart by so-called spacers and the volume thus obtained is filled with a liquid crystal composition. The orientation of the liquid crystal molecules therein is determined by an interaction with the anisotropically oriented polymer molecules in the liquid crystal alignment layer. Upon application of an electric field, the orientation of the liquid crystal molecules can be switched from one orientation to another, and a modulation of the light output through crossed polarisers is thereby obtained.

Generally, the substrates in LCDs consist of glass. At present, several key display technologies are being developed in the industry to make flexible displays wherein plastic foils can be used as a substrate. A truly flexible display should not contain inorganic layers on the plastic substrate, since the brittleness of inorganic compositions causes the formation of defects upon bending the display. As a replacement of indium-tin oxide (ITO), the most commonly used electroconductive composition, conducting polymers such as polythiophene can be used. Such replacement of inorganic layers by organic equivalents enables the use of cheaper, easier-to-build, roll-to-roll coating methods for making flat panel displays.

The liquid crystal alignment layers in most of today's LCDs are oriented polyimide (PI) layers. Known since the very beginning of LCD technology, these PI layers have remained essentially unchanged

- 3 -

for 25 years. The method of making PI alignment layers is complex and requires careful control of many parameters which may affect the final quality of the display. Typically, the following steps are needed to obtain a PI alignment layer : (1) cleaning the substrate, effected through a sequence of several substeps such as supersonic washing in aqueous solutions, rinsing, supersonic washing in pure water, rinsing, supersonic washing in an organic solvent, blowing with nitrogen, drying, and finally UV photocleaning; (2) spin coating the PI precursor (a solution of PI monomers in an organic solvent) and baking to cure the coated layer, typically at a temperature between 200 and 350 °C; and (3) orientation of the PI molecules by stretching or shearing techniques, or more preferably, by rubbing with a rayon, cotton or velvet cloth. The baking step is generally performed in vacuo, otherwise the PI alignment layer does not adhere well to the substrate and may be disrupted during rubbing, especially at the areas of the patterned electroconductive layer at which the ITO layer has been etched out.

The high temperature required during the baking step as well as the use of various organic solvents renders these prior art methods incompatible with many plastic substrates. Other problems are associated with the low stability of the PI precursor (must be stored at low temperature) and the disposal of organic solvents and other chemicals which are necessary in these conventional methods. Especially the build-up of electrostatic charges in the PI layer, e.g. during rubbing, is a serious problem as dust particles are attracted thereby, which, once trapped in the display cell, may cause poor alignment, severe wedging of the substrates or electrical breakdown by short circuiting across the dust particle.

In order to solve these problems, alternative methods have been described to obtain LCD alignment layers. Photo-alignment methods such as the anisotropical cross-linking of poly(vinyl cinnamate) and PI films by exposure to linearly polarised UV light have been described (Applied Physics Letters, Vol. 73, p. 3372, 1998). Such methods are also suitable for aligning polythiophene layers, but are not a suitable alternative for conventional PI layers because of their thermal instability. The problem of electrostatic charge generation may also be solved by making electroconductive alignment layers as described in US 5,639,398. In the latter patent, a viscous

- 4 -

lyotropic polyaniline solution is coated on ITO and then oriented by shearing with a blade of a knife or a glass plate. While drying, the liquid crystalline polyaniline molecules retain their orientation. However, the conductivity values of the polyaniline layer reported in 5,639,398 are low, so ITO is still needed as an electrode layer. In addition, it is mentioned therein that polythiophene is not suitable for such a liquid crystalline polymer alignment method.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a liquid crystal alignment layer which may be obtained by a simple, convenient method that operates at low temperature, and does not require the use of organic solvents or other hazardous chemicals. This object is obtained according to the present invention by the layer defined in claim 1.

It is a further object of the present invention to provide an electroconductive liquid crystal alignment layer so that alignment by rubbing does not generate a build-up of electrostatic charges. This object is obtained according to the present invention by the material defined in claim 2.

Specific features for preferred embodiments of the invention are defined in the dependent claims.

Further advantages and embodiments of the present invention will become apparent from the following description.

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, it has been found that an oriented polythiophene containing layer is capable of aligning liquid crystal molecules just as the well-known PI liquid crystal alignment layers. Contrary to PI, the polythiophene containing layer can be obtained by coating from an aqueous solution and does not require baking at high temperatures. Also contrary to a PI-precursor, an (aqueous) polythiophene dispersion shows good long-term stability and the polythiophene layer is resistant to a wide variety of organic solvents such as propanole, acetone, buthyl acetate, 1-methoxy-2-propanole, and cyclo-pentanone. By doping the

polythiophene with a polyanion as described below, a layer can be obtained with a high electroconductivity so that no dust particles are attracted by the layer. As a particular advantage of the present invention, the electroconductivity of such a polythiophene liquid crystal orientation layer is sufficiently high so that it can also be used as an electrode for switching the liquid crystal phase of an LCD. The combined use of a layer according to the present invention as both an electrode and a liquid crystal alignment layer significantly reduces the cost of LCD manufacturing and enables the development of all-organic, flexible displays.

Before setting out the elements of the present invention, some terms of the appending claims will be defined. The term "oriented polymer layer" defines a layer which comprises a polymer, and optionally other ingredients, wherein some or all of the polymer molecules have been anisotropically oriented into a particular direction. The term "support" is used in the meaning of a "self-supporting material" so as to distinguish it from a "layer" which may be coated on a support but which is not self-supporting.

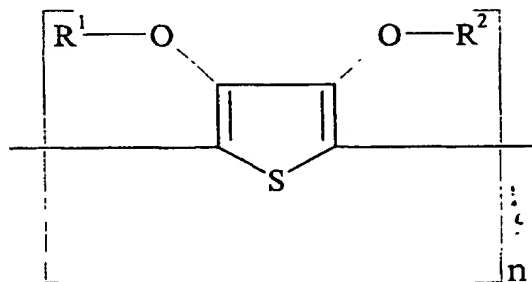
The term "electroconductive" is related to the electric resistivity of the material. The electric resistivity of a layer is generally expressed in terms of surface resistivity R_s (unit Ω ; often specified as Ω/\square). Alternatively, the electroconductivity may be expressed in terms of volume resistivity $R_v = R_s \cdot d$, wherein d is the thickness of the layer, or in units of conductance $k_i = 1/R_i$ ($i=s,v$; unit=S(iemens)= $1/\Omega$). $10^5 \Omega/\square$ is typically regarded as a value of surface resistivity which distinguishes electroconductive materials from anti-static materials. So to term "electroconductive" as used herein should be interpreted as "having a surface resistivity below $10^5 \Omega/\square$ ". Anti-static materials typically have a surface resistivity in the range from 10^6 to $10^{11} \Omega/\square$ and cannot be used as an electrode.

All values of electric resistivity presented herein are measured according to the following method. The support coated with the electroconductive layer is cut to obtain a strip having a length of 27.5 cm and a width of 35 mm. Over the width of the strip electrodes are applied at a distance of 10 cm. The electrodes are made of a conductive polymer, ECCOCOAT CC-2 available from Emerson & Cumming Speciality polymers. Over said electrode a constant

- 6 -

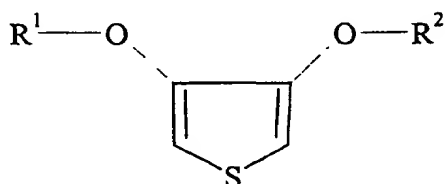
potential is applied and the current flowing through the circuit is measured on a Pico-amperemeter KEITHLEY 485. From the potential and the current, taking into account the geometry of the area between the electrodes, the surface resistivity in Ω/\square is calculated.

The polythiophene used in the present invention has preferably the following formula :



wherein R^1 and R^2 each independently represent hydrogen or a C_1 - C_4 alkyl group or together represent an optionally substituted C_1 - C_4 alkylene group or cycloalkylene group, preferably an ethylene group, an optionally alkyl-substituted methylene group, or an optionally C_1 - C_{12} alkyl- or phenyl-substituted 1,2-ethylene group, 1,3-propylene group or 1,2-cyclohexylene group. Poly(3,4-ethylenedioxy-thiophene) is highly preferred.

The preparation of such a polythiophene and of aqueous dispersions containing such a polythiophene are described in EP-A-440 957 and corresponding US Patent 5,300,575. Basically, the preparation of the polythiophenes indicated above proceeds by oxidative polymerisation of 3,4-dialkoxythiophenes or 3,4-alkylenedioxythiophenes according to the following formula :



wherein R^1 and R^2 are as defined above.

In order to obtain high electroconductivity, said polythiophene is preferably doped by carrying out said polymerisation in the presence of a polyanion compound or a polyacid or salt thereof which may form a polyanion, as described in EP-A-440 957. Due to the presence of said polyanion, the polythiophene is positively doped, the location and number of the positive charges being not deter-

minable with certainty and therefore not mentioned in the above formula of the repeating units of the polythiophene polymer. Preferred polyacids or salts thereof are polymeric carbonic acids such as poly(acrylic acid), poly(methacrylic acid) and poly(maleic acid) or polymeric sulphonic acids such as poly(styrene sulphonic acid) or poly(vinyl sulphonic acid). Alternatively, copolymers of such carbonic and/or sulphonic acids and of other polymerisable monomers such as styrene or acrylates can be used. Poly(styrene sulphonic acid) is especially preferred. The molecular weight of these polyanion forming polyacids is preferably between 1000 and 2×10^6 , more preferably between 2000 and 5×10^5 . These polyacids or their alkali salts are commercially available and can be prepared according to the known methods, e.g. as described in Houben-Weyl, Methoden der Organische Chemie, Bd. E20 Makromolekulare Stoffe, Teil 2, (1987), pp. 1141.

Stable aqueous polythiophene dispersions having a solids content of 0.05 to 55% by weight and preferably of 0.1 to 10% by weight can be obtained by dissolving a thiophene corresponding to the formula above, a polyacid or salt thereof and an oxidising agent in an organic solvent or preferably in water, optionally containing a certain amount of organic solvent, and then stirring the resulting solution or emulsion at 0 to 100°C until the polymerisation reaction is completed. The oxidising agents are those which are typically used for the oxidative polymerisation of pyrrole as described in for example J. Am. Soc., Vol. 85, p. 454 (1963). Preferred inexpensive and easy-to-handle oxidising agents are iron(III) salts, e.g. FeCl_3 , $\text{Fe}(\text{ClO}_4)_3$ and the iron(III) salts of organic acids and inorganic acids containing organic residues. Other suitable oxidising agents are H_2O_2 , $\text{K}_2\text{Cr}_2\text{O}_7$, alkali or ammonium persulfates, alkali perborates, potassium permanganate and copper salts such as copper tetrafluoroborate. Air or oxygen can also be used as oxidising agents. Theoretically, 2.25 equivalents of oxidising agent per mole of thiophene are required for the oxidative polymerisation thereof (J. Polym. Sci. Part A, Polymer Chemistry, Vol. 26, p.1287, 1988). In practice, however, the oxidising agent is preferably used in excess, for example in excess of 0.1 to 2 equivalents per mole of thiophene.

- 8 -

The polythiophene dispersions obtained according to the above method can then be used as basic ingredient of a solution which can be coated on a support and the coated layer thus obtained can be oriented as described below so as to make the material of the present invention, which comprises an oriented polythiophene layer on a support. The coating solution may also comprise additional ingredients, such as one or more binders, one or more surfactants, spacing particles, UV-filters or IR-absorbers. Suitable polymer binders are described in EP-A 564 911. Such binders may be treated with a hardening agent, e.g. an epoxysilane as described in EP-A 564 911, which is especially suitable when coating on a glass support.

The coating solution can be applied to the support by any means known in the art : it can be spin-coated, sprayed or coated by any of the continuous coating techniques that are used to coat solutions on running webs or sheets, e.g. dip coating, rod coating, blade coating, air knife coating, gravure coating, reverse roll coating, extrusion coating, slide coating and curtain coating. An overview of these coating techniques can be found in the book "Modern Coating and Drying Technology", Edward Cohen and Edgar B. Gutoff Editors, VCH publishers, Inc, New York, NY, 1992. It is also possible to coat simultaneously multiple layers by coatings technique such as slide coating and curtain coating. It is also possible to apply the coating solution to the support by printing techniques, e.g. jet printing, screen printing, gravure printing, flexo printing, or offset printing.

Polythiophene layers having a high electroconductivity can be obtained by adding to the coating solution an organic compound containing two or more radicals selected from the group consisting of hydroxy, carboxy or an amide or lactam group, as described in EP-A-686 662. Typical useful compounds are e.g. N-methyl-2-pyrrolidone, 2-pyrrolidone, 1,3-dimethyl-2-imidazolidone, N,N,N',N'-tetramethylurea, formamide, dimethylformamide, and N,N-dimethylacetamide. Highly preferred examples are sugar or sugar derivatives such as arabinose, saccharose, glucose, fructose and lactose, or di- or polyalcohols such as sorbitol, xylitol, mannitol, mannose, galactose, sorbose, gluconic acid, ethylene glycol, di- or tri(ethylene glycol), 1,1,1-trimethylol-propane, 1,3-propanediol, 1,5-pentanediol, 1,2,3-propanetriol, 1,2,4-butanetriol, 1,2,6-

hexanetriol, or aromatic di- or polyalcohols such as resorcinol. The amount of these compounds in the coated layer may be between 10 and 5000 mg/m², preferably between 50 and 1000 mg/m².

The coating solution is preferably applied to the support in such an amount that the coated layer contains between 10 and 5000 mg of polythiophene per m², more preferably between 100 and 500 mg of polythiophene per m². Preferably, the coated layer has a surface resistivity below 10⁵ Ω/□, more preferably below 10⁴ Ω/□ and even more preferably below 10³ Ω/□. A highly preferred method for obtaining polythiophene layers with a surface resistivity of less than 10³ Ω/□ is described in EP-A no. 98203951, filed on 17.11.1998.

The support used in the materials of the present invention can be inorganic or organic. Suitable polymeric films are made of e.g. a polyester such as poly(ethylene terephthalate) (PET), poly(ethylene naphthalate) (PEN), polystyrene, polyethersulphone (PES), polycarbonate (PC), polyacrylate, polyamide, polyimides, cellulose triacetate, polyolefines, polyvinylchloride, cyclo-olephine (co-)polymers such as polydicyclopentadiene (PDCP). PET, PEN, PES, PC and PDCP are highly preferred. As inorganic supports can be used silicon, ceramics, oxides, polymeric film reinforced glass or, more preferably, glass or glass/plastic laminates, e.g. laminates as described in WO 99/21707 and WO 99/21708.

The polythiophene layer may be applied directly on the support, but, preferably, one or more intermediate layers are present between the support and the polythiophene layer. The support is preferably provided with an adhesion-improving so-called anchor layer, whereon the above described coating solution can be applied. Such an anchor layer may be present at either side of the support. Preferred anchor layers also act as a passivating layer, i.e. have barrier properties with regard to compounds which may diffuse from the support, e.g. unreacted monomer in case of a plastic support, into the liquid crystal alignment layer or other layers provided on the support. Such a passivating anchor layer comprises e.g. a cured polyimide or polyacrylate. A preferred passivating anchor layer comprises polyvinylalcohol and a silica dispersion, e.g. those supplied by Bayer AG, Leverkusen, West-Germany under the tradename KIESELSOL. Said polyvinylalcohol/silica layer is preferably cured, e.g. by

- 10 -

adding a tetra-alkoxysilane such as tetramethylorthosilicate and tetraethylorthosilicate.

Other layers which may be present between the polythiophene layer and the support include UV filter layers, colour filter layers and transparent electroconductive layers such as ITO. Said UV filter layer is preferably applied at the back side of the material of the present invention, i.e. at the side opposite to the polythiophene layer. Especially when the oriented polythiophene layer of the present invention is not or not sufficiently electroconductive, it may be necessary to include an ITO layer between the support and the oriented polythiophene layer. The material of the present invention may also contain barrier layers which prevent the diffusion of oxygen and/or water vapour through the support. Preferred barrier layers for use to this end include the known vacuum-deposited metal or metal oxide layers, e.g. SiO_x layers, or the so-called organically modified ceramic layers, as described in Coating, no. 9/98, p.314 and 10/97, p.358, and the poly(hydroxy amide ethers) described in Macromolecules, vol.31, p.8281 (1998). A combination of a SiO_x layer and an organically modified ceramic layer is especially preferred.

Taking all the above into account, a specific example of a material according to the present invention comprises the following layers (in the order given) :

- an oriented polythiophene liquid crystal alignment layer
- a transparent electroconductive layer (e.g. ITO)
- a passivating anchor layer
- a support
- an anchor layer
- an SiO_x barrier layer
- an organically modified ceramic as a second barrier layer.

LCDs are generally driven by a patterned (row/column) electroconductive layer, defining a pixel at each row-column overlap. According to a preferred embodiment of the present invention, the oriented polythiophene liquid crystal alignment layer is characterised by a surface resistivity of less than $10^4 \Omega/\square$, or even less than $10^3 \Omega/\square$, so that said layer can also be used as an electrode layer for most LCD applications and, as a result, the use of a separate ITO layer is not necessary. So in a preferred embodiment, the oriented polymer layer of the present invention is a

patterned, non-continuous electrode layer, which simultaneously acts as a liquid crystal alignment layer.

Several techniques are known in the art to obtain a patterned polythiophene layer. A first technique involves the image-wise application of a polythiophene paste by e.g. screen printing electrode paths as described in WO 99/34371. WO97/18944 describes another suitable process wherein a positive or negative photoresist is applied on top of a layer of an organic electroconductive polymer, such as polythiophene, and after the steps of selectively exposing the photoresist to UV light, developing the photoresist, etching the electroconductive polymer layer with an oxidative agent such as ClO^- and finally stripping the non-developed photoresist, a patterned layer is obtained. A similar technique has been described in Synthetic Metals, 22 (1988), p. 265-271 for the design of an all-organic thin-film transistor. Research Disclosure No. 1473 (1998) describes photoablation as a method suitable for patterning organic electroconductive polymer layers, wherein the selected areas are removed from the substrate by laser irradiation.

A problem associated with the above patterning methods is the fact that no layer is present at the non-conducting areas (has been removed by etching or ablation or has not been applied from the start), so the liquid crystals can only be aligned at the conducting areas. Therefore, patterning methods are preferred wherein the non-conducting areas are not removed but 'de-activated', i.e. rendered non-conductive, e.g. by oxidation of the polythiophene. Having a similar layer thickness at conducting as well as non-conducting areas is also beneficial when the layer needs to be overcoated with very thin layers (no substantial step formation at the borders between conducting and non-conducting areas). Preferred patterning methods wherein the polythiophene is not removed at non-conducting areas include the one described in EP-A no. 99202705, filed on 23.08.1999, wherein a layer containing a polythiophene, a polyanion and a di- or polyhydroxy organic compound has a surface resistivity higher than $10^4 \Omega/\square$, which can be reduced to a value which is 10 to 10^5 times lower by heating selected areas without substantially ablating or destroying the polymer layer. Finally, another suitable method involves the image-wise application of an oxidising composition to an electroconductive polythiophene layer, e.g. by

- 12 -

screen printing a ClO^- containing paste, as described in EP-A no. 99201645, filed on 20.05.1999. Although the layer thickness may be reduced slightly by the oxidation treatment, the conducting and non-conducting areas have a comparable layer thickness.

The polythiophene containing layer can be oriented by similar techniques as used for making PI liquid crystal alignment layers. In a preferred method, a rotating screen printing roller provided with a velvet surface is translated over the polythiophene containing layer so as to apply a rolling friction on the surface of the layer. Parameters which influence the result (e.g. the so-called pre-tilt of the liquid crystal molecules) are the number of rubbing cycles, the contact length, the applied pressure which can be set by adjusting the distance between the roller and the layer surface (so-called pressure-depth), the radius of the roller, the rotation speed of the roller and the translation speed of the roller relative to the surface of the layer. These parameters can be controlled by using a screen printing apparatus according to the specifications of the supplier of the rubbing cloth and equipment. Other methods are also suitable, e.g. moving a carbon fibre brush or a doctor blade provided with a velvet or cotton cloth over the layer.

The present invention can be used for the manufacturing of passive-matrix LCDs as well as active-matrix LCDs such as thin-film-transistor (TFT) displays. Particular examples are twisted nematic (TN), supertwisted nematic (STN), double supertwisted nematic (DSTN), retardation film supertwisted nematic (RFSTN), ferro-electric (FLC), guest-host (GH), polymer-dispersed (PF), polymer network (PN) liquid crystal displays, and so on.

Example

Preparation of a polythiophene dispersion (hereinafter referred to as "PT")

Into 3000 ml of an aqueous solution of 31.5 g of poly-styrene sulphonic acid (171 mmole of SO_3H groups) with number-average molecular weight (M_n) 40000, were introduced 25.7 g of sodium peroxodisulfate ($\text{Na}_2\text{S}_2\text{O}_8$), 0.225 g of $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and 12.78 g of 3,4-ethylenedioxy-thiophene. The thus obtained reaction mixture was

stirred vigorously for 7 hours at 30 °C. After adding again 4.3 g of sodium peroxodisulfate ($\text{Na}_2\text{S}_2\text{O}_8$) the mixture was vigorously stirred during 14 hours at 30 °C. The reaction mixture was then stirred twice during 2 hours at room temperature in the presence of a granulated weak basic ion exchange resin LEWATIT H 600 and strongly acidic ion exchanger LEWATIT S 100 (both trade names of Bayer AG, Leverkusen, Germany). The ion exchange resins were then filtered off and, finally, the mixture was post-heated at 95°C for 2 hours. The resulting dark blue dispersion had a solid content of 1.15 % by weight.

Coating of the polythiophene layer

417 ml of the above dispersion PT was mixed with a binder (8.5 ml of a 300 g/l aqueous dispersion of a copolymer of 88% vinylidene-chloride, 10% methylacrylate and 2% itaconic acid) and 50 g of N-methylpyrrolidone. Then, a surfactant was added (0.5 ml of FLUORAD FC430, trade name of 3M) and finally distilled water to make 1 litre. The solution thus obtained was coated at a wet thickness of 40 μm on a 100 μm PES film and then dried at 35 °C. The coated layer comprised 200 mg/m^2 of poly(3,4-ethylenedioxy-thiophene) doped with poly(styrene sulphonate). The thickness and surface resistivity of the layer were 0.2 μm and 600 Ω/\square respectively, i.e. the conductance k_v was $1/(600 \Omega)/(0.2 \times 10^{-4} \text{ cm}) = 83 \text{ S}/\text{cm}$.

Patterning of the polythiophene layer

The above material was cleaned with a high-pressure water jet. Then a conventional photoresist layer of 1.4 μm thickness was spin-coated on the polythiophene layer and soft-baked at 120 °C during 10 min. The photoresist was then exposed through a mask film containing an image of five segments of different sizes, developed and hard-baked at 120 °C during 10 min. The material was dipped during 1 min. in a 12 wt.% solution of NaOCl to oxidise the polythiophene areas which were not covered by the photoresist layer. The oxidised areas are not removed by this treatment but 'de-activated' (rendered non-conductive). After rinsing with water, the photoresist was stripped with an acetone/isopropylalcohol 1:1 (vol.) mixture during 10 min.

- 14 -

followed by another treatment with isopropylalcohol during 10 min. The material was then cleaned with a high-pressure water jet.

Rubbing of the patterned polythiophene layer

The patterned polythiophene layer was oriented with equipment supplied by Hornell-Automation (Sweden), type MELP RM-RR 400 Rub/Dry Cleaner. A velvet roller having a diameter of 120 mm, rotating at 800 rpm, was translated once over the polythiophene layer at a translation speed of 600 mm/min and a rubbing pressure depth of 100 μm .

Assembly of a passive TN LCD cell

Two of the above substrates were assembled to form a liquid crystal display cell by plotting a glue frame, spinning-on 5 μm spacer pearls, pressing the substrates into contact and UV-curing the glue frame. The cell was then filled with conventional twisted nematic LC material and sealed. Finally, crossed polariser sheets were laminated to the cell.

By applying the driving voltage to the above cell in front of a backlight, it was shown that the five segments could be switched without any cross-talk between the segments (sharp edges). A good normally white orientation of the TN material was obtained in the non-oxidised polythiophene areas.

THIS PAGE BLANK

15. 10. 1999

(54)

- 15 -

[CLAIMS]

1. An oriented polymer layer which is suitable as a liquid crystal alignment layer, characterised in that said polymer is a polythiophene.
2. An oriented polymer layer according to claim 1 further comprising a polyanion and characterised by a surface resistivity lower than $10^5 \Omega/\square$.
3. A material comprising an oriented polymer layer according to claim 1 or 2 on a support, wherein the support consists essentially of poly(ethylene terephthalate), poly(ethylene naphthalate), polycarbonate, polydicyclopentadiene, poly(ether sulphone), glass or a glass/plastic laminate.
4. A material according to claim 3 further comprising an indium-tin oxide layer between the support and the oriented polymer layer.
5. A material according to claims 3 or 4 further comprising a passivating anchor layer between the support and the oriented polymer layer.
6. A material according to any of claims 3 to 5 further comprising a barrier layer.
7. A method of making a liquid crystal alignment layer comprising the step of orienting by mechanical means a layer which comprises a polythiophene.
8. A method according to claim 7 wherein the layer further comprises a polyanion and is characterised by a surface resistivity lower than $10^5 \Omega/\square$.
9. A method according to claim 7 or 8 wherein the liquid crystal alignment layer is a patterned layer consisting of conducting and non-conducting areas.

- 16 -

10. A method according to claim 9 wherein the liquid crystal alignment layer is not removed, at non-conducting areas.
11. A liquid crystal display comprising a liquid crystal alignment layer according to claim 1 or 2 or a material according to any of claims 3 to 6.
12. Use of a layer comprising an oriented polythiophene and optionally a polyanion as a liquid crystal alignment layer.

15. 10. 1999

[ABSTRACT]

(54)

LIQUID CRYSTAL ALIGNMENT LAYER

A rubbed polythiophene layer is provided which can be used as a liquid crystal alignment layer of an LCD. According to a preferred embodiment, a polythiophene layer having a surface resistivity lower than $10^5 \Omega/\square$ is used as both an electrode layer and a liquid crystal alignment layer. Contrary to the generally used polyimide layers, the polythiophene liquid crystal alignment layer can be obtained by simple, cold processes and due to the electroconductivity of the polythiophene, no dust is attracted during rubbing.

THIS PAGE BLANK (USPTO)